

# Preparation of palladium nanoparticles–titanium electrodes as a new anode for direct methanol fuel cells

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**Abstract** Pd nanoparticle/Ti electrodes are prepared by electroless plating of palladium on titanium plates. The morphology and surface analysis of Pd nanoparticle/Ti electrodes are investigated using scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. The results indicate that palladium nanoparticles are homogeneously deposited on the surface of titanium plates. The electro-catalytic activity of Pd nanoparticle/Ti electrodes in the methanol electro-oxidation is studied by cyclic voltammetry and chronoamperometry methods. The results show that the electro-catalytic oxidation of methanol on the Pd nanoparticle/Ti electrode improved compare to pure palladium electrode and confirmed the better electro-catalytic activity and stability of these new electrodes.

**Keywords** Methanol electro-oxidation · Palladium nanoparticle · Titanium plate

## Introduction

Direct alcohol fuel cells employing alcohols directly as fuel, are attractive as power sources for mobile, stationary, and portable applications. The alcohol is fed directly into the fuel cell without any previous chemical modification and is oxidized at the anode while oxygen is reduced at the cathode. This feature avoids problems related to production, purification, and storage of hydrogen [1–3]. While methanol offers the advantage of easy storage and transportation

when compared to hydrogen oxygen fuel cell, its energy density and operating cell voltage are lower than the theoretical energy density and the thermodynamic potential [1, 4]. The performance of direct alcohol fuel cells has improved markedly in the past several years. High activity of alcohols oxidation on platinum makes it a suitable electro-catalyst for the direct methanol fuel cells (DMFC) anode. However, it has been conclusively shown that platinum could affect the anode activity by greatly poisoning carbon monoxide. Palladium is much cheaper than platinum, and if it has the same activity for alcohols electro-oxidation, palladium may have a promising future. In order to reduce the amount of noble metal loading and also for enhancement of electro-catalytic activity of electrodes, there have been considerable efforts to increase the dispersion of the metal particles on the different supports. The titanium is corrosion resistant, has a high mechanical strength, a reasonable cost, wide electrochemical potential windows, and good stability. Because of its excellent properties, titanium has been applied as a substrate in order to prepare novel and stable electro-catalysts including the well-known DSA electrode [5–7]. The titanium-supported catalysts present significant electro-catalytic activity towards the methanol oxidation [8–11]. Compared with the conventional structure of the anode, the titanium anode has many advantages [12] such as simplicity, easily produced on a mass scale, low cost, and allowing flexibility in terms of shape. Titanium anodes prepared by deposition of the platinum directly on the titanium have been used in a DMFC and show a higher performance than platinum supported on carbon black [13–16]. To the best of our knowledge, the electro-oxidation of methanol on titanium-coated with noble metals is only reported in some articles in the literature [17–19]. In the present work, for the first time, we prepared a high activity electro-catalyst based on the

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deposition of palladium nanoparticle on titanium plate and studied their electrochemical activity for methanol oxidation using cyclic voltammetry and chronoamperometry methods.

## Experimental

### Chemicals and solutions

All aqueous solutions were prepared with distilled water, and all compounds were of analytical grade and used without further purification.

### Electrochemical cells, instrumentation, and electrodes

All electrochemical experiments were carried out in a conventional three-electrode cell. The measuring equipment was carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical system run by Powersuite software. The reference electrode was a saturated calomel electrode. A platinum plate of geometric area approximately 20 cm<sup>2</sup> was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel reference electrode.

### Preparation of Pd nanoparticle/Ti electrodes

Titanium disks were cut from a titanium plates (purity 99.99%, 1 mm diameter) and mounted using polyester resin. The titanium electrodes was first mechanically polished with different emery type abrasive papers, rinsed in a bath of distilled water, and then chemically etched by immersing in a mixture of HF (50 wt.%):HNO<sub>3</sub> (65 wt.%) 1:3 solution for 1 min. Prior to electrodeposition, titanium samples were degreased by sonicating in acetone and ethanol followed by rinsing with distilled water. Palladium nanoparticles were deposited on the prepared titanium plates by electroless method. The sensitizing–activating treatment was carried out by soaking them first in 0.0045 mol l<sup>-1</sup> SnCl<sub>2</sub> solution for 5 min and then in 0.00059 mol l<sup>-1</sup> PdCl<sub>2</sub> solution for 5 min at room temperature. The samples were then rinsed with distilled water and soaked in the electroless-plating bath containing 0.01 mol PdCl<sub>2</sub>, 4.8 g l<sup>-1</sup> of ethylene-diamine as a complexing agent, and 11 g l<sup>-1</sup> of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O as a reducing agent, while pH value was adjusted to 8. The reaction temperature was 323 K. Electroless deposition of palladium on titanium plates was performed in various times and finally it was observed that 8 min is the optimum time, resulting in highest current values for methanol oxidation. After the electroless plating, the samples were rinsed, dried, and subjected to the characterization. The final palladium

loading, as measured by dissolution of the deposit followed by ICP analysis was about 1.8 mg cm<sup>-2</sup>.

### Structure characterization

Morphology, alignment, and composition of palladium nanoparticles deposited on the titanium plate were characterized with a scanning electron microscope (Philips, Model XL30) and energy-dispersive X-ray spectroscopy (EDX).

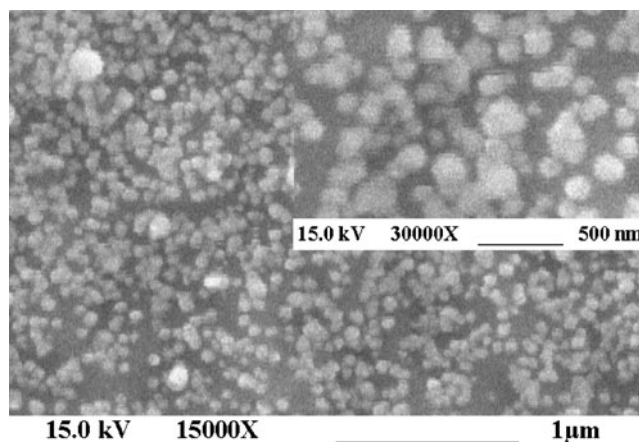
## Results and discussion

### Morphology of Pd nanoparticle/Ti electrodes

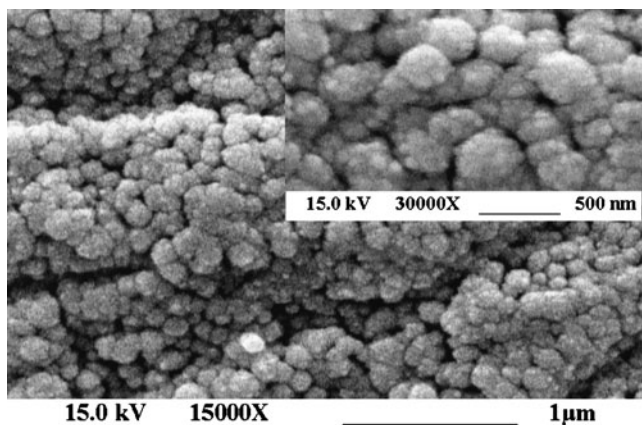
Figure 1 shows the SEM micrographs of titanium electrodes after sensitizing–activating treatment by soaking them first in 0.0045 mol l<sup>-1</sup> SnCl<sub>2</sub> solution for 5 min and then in 0.00059 mol l<sup>-1</sup> PdCl<sub>2</sub> solution for 5 min at room temperature. Figure 2 shows palladium nanoparticles deposited on the titanium plate. It can be seen that agglomerations containing smaller particles (smaller 5 nm) that formed from combination with others particles and have size about 30–50 nm, are distributed in an almost homogeneous manner at the surface of the titanium plate. Figure 3 shows the EDX spectrum of palladium nanoparticles/Ti electrodes. EDS result confirms the presence of palladium nanoparticles on the titanium palates.

### Characterisation of the Pd nanoparticle/Ti electrode surface

To determine whether the electroless deposition procedure had resulted in the removal of the oxide layer, thereby ensuring good electrical contact between the palladium

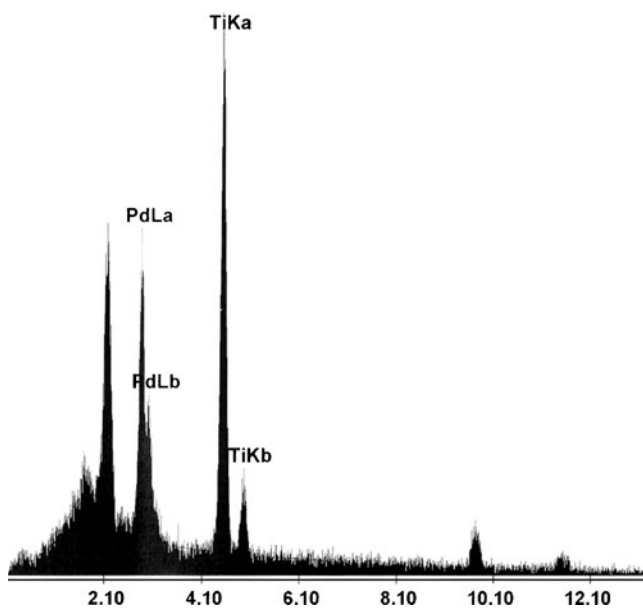


**Fig. 1** The surface morphology of titanium electrodes after sensitizing–activating treatment by soaking them first in 0.0045 mol l<sup>-1</sup> SnCl<sub>2</sub> solution for 5 min and then in 0.00059 mol l<sup>-1</sup> PdCl<sub>2</sub> solution for 5 min at room temperature

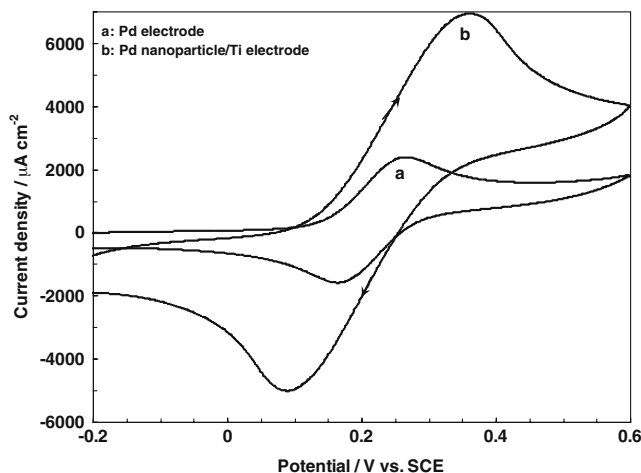


**Fig. 2** The surface morphology of palladium nanoparticles deposited on the titanium plate

deposit and the underlying substrates, the palladium nanoparticles/Ti were tested as electrodes using a one electron redox couple. Figures 4 and 5 show the voltammetric curves for the reduction of  $K_3Fe(CN)_6$  on flat palladium, palladium nanoparticles/Ti, and titanium electrodes. The voltammogram for the palladium nanoparticles/Ti electrodes shows the expected reversible behavior for the reduction on a bulk palladium electrode (Fig. 4). In comparison, the voltammogram obtained with one titanium electrode shows increased peak separation and peak widths (Fig. 5). This is probably attributable to a passivating surface film, most likely the oxide layer present on the surface of the titanium electrode. On exposure to air, a thin titanium oxide film is formed on the surface of a titanium layer. This could grow thicker, as well as becoming a

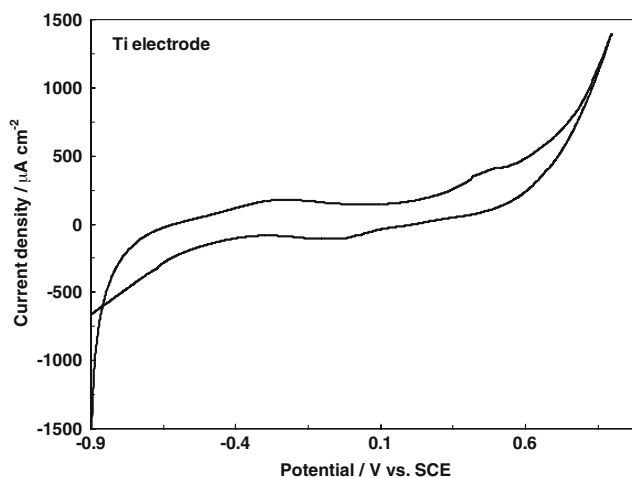


**Fig. 3** An EDX of palladium nanoparticles/Ti electrodes



**Fig. 4** Cyclic voltammograms for palladium nanoparticles/Ti and palladium electrodes recorded at  $100 \text{ mV s}^{-1}$  in a solution containing  $10 \text{ mM } K_3[Fe(CN)_6]$  in  $1 \text{ M KCl}$  at  $25 \text{ }^\circ\text{C}$

titanium oxide layer when using titanium as an electrode, due to electrochemical or chemical oxidation. The presence of such a passivating layer which would shift the position of the peaks for the redox reaction of the ferri/ferrocyanide to greater overpotentials, increasing peak separation and reducing peak heights, as observed. The lack of such resistances and overpotentials observed on repeated redox cycling of the palladium nanoparticles/Ti electrodes indicates that there is no significant resistive film between the underlying titanium and the deposited palladium film. It suggests that the adhesion and electrical contact property of the deposited palladium film with titanium is quite satisfactory and because high surface area of palladium nanoparticles/Ti electrode, the current density are much more than the pure palladium electrode.



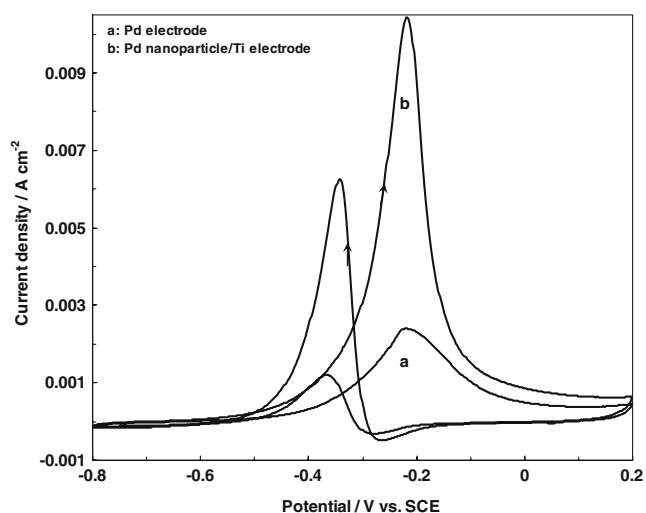
**Fig. 5** Cyclic voltammograms for a titanium electrode which was fabricated then left in an oxygenated environment at  $100 \text{ mV s}^{-1}$  in a solution containing  $10 \text{ mM } K_3[Fe(CN)_6]$  in  $1 \text{ M KCl}$  at  $25 \text{ }^\circ\text{C}$

### Electro-catalytic activity of Pd nanoparticle/Ti and flat palladium electrodes for methanol electro-oxidation

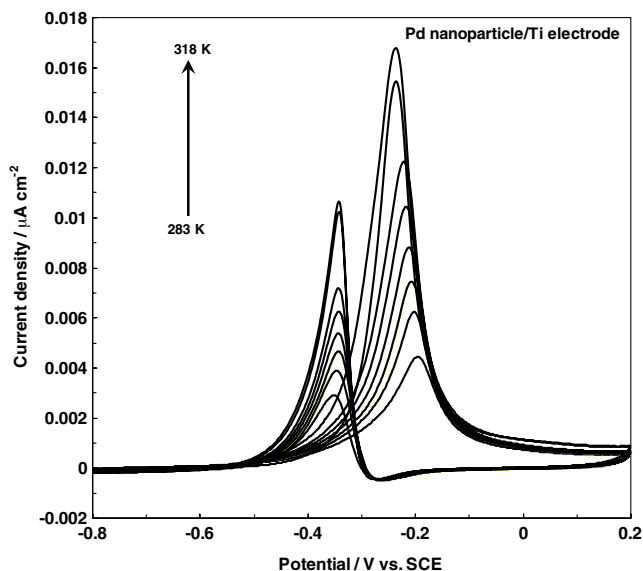
In order to compare palladium nanoparticles/Ti electrode with flat palladium electrode, the cyclic voltammetry method was used to estimate the electro-catalytic behavior of the electrodes. Figure 6 presents cyclic voltammograms of flat palladium and palladium nanoparticles/Ti electrodes in 1.0 M NaOH+0.1 M methanol aqueous solutions, at a scan rate of  $100 \text{ mV s}^{-1}$ . It can be seen from Fig. 6 that the current density for methanol oxidation on Pd nanoparticle/Ti electrode is greater than that observed for flat palladium electrode, indicating the surface area of Pd nanoparticle/Ti electrode was enlarged by dispersion palladium nanoparticles on the surface of titanium palates.

### Effect of medium temperature

Temperature is one of the most important factors affecting the reaction rate. The effect of medium temperature on the electro-oxidation of methanol on flat palladium electrode and Pd nanoparticle/Ti electrode was investigated in the temperature range of 283–318 K by the method of cyclic voltammetry. Figure 7 shows the cyclic voltammograms of methanol oxidation on the surface of Pd nanoparticle/Ti electrode at different temperatures. It can be seen that an increase in temperature caused (I) an evident increase in the anodic peak current for methanol oxidation up to  $45^\circ\text{C}$ , indicating acceleration of methanol oxidation kinetics with temperature and (II) a negative shift in the onset potential and a positive shift in the re-oxidation peak potential was observed. This phenomenon is attributed to the increase in the rate of charge transfer at electrode/electrolyte interface.



**Fig. 6** Cyclic voltammograms for a flat palladium electrode (a) and palladium nanoparticles/Ti electrode (b) in a 1.0 M NaOH+0.1 M methanol aqueous solution at  $25^\circ\text{C}$  with a scan rate of  $100 \text{ mV s}^{-1}$

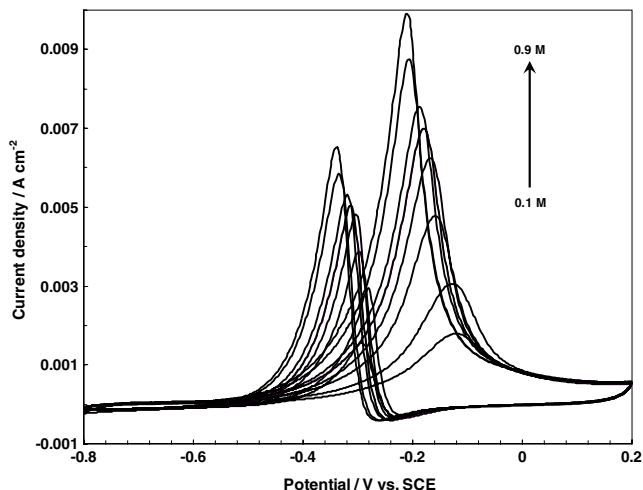


**Fig. 7** The cyclic voltammograms of palladium nanoparticles/Ti electrode in 1 M NaOH+0.1 M methanol aqueous solutions at different temperatures with scan rate of  $100 \text{ mV s}^{-1}$

At the same time, high temperature will decrease the increases diffusion phenomena, so higher electro-oxidation currents could be obtained.

### Effect of NaOH concentration

Since the value of pH affects the methanol oxidation on Pd nanoparticle/Ti electrode, it is important to study the effect of NaOH concentration on methanol oxidation. The effect of NaOH concentration on methanol oxidation on Pd nanoparticle/Ti electrode was studied in 0.1 M methanol with different NaOH concentration and the results are depicted in Fig. 8. One can see that a higher NaOH concentration results in a lower oxidation peak potential

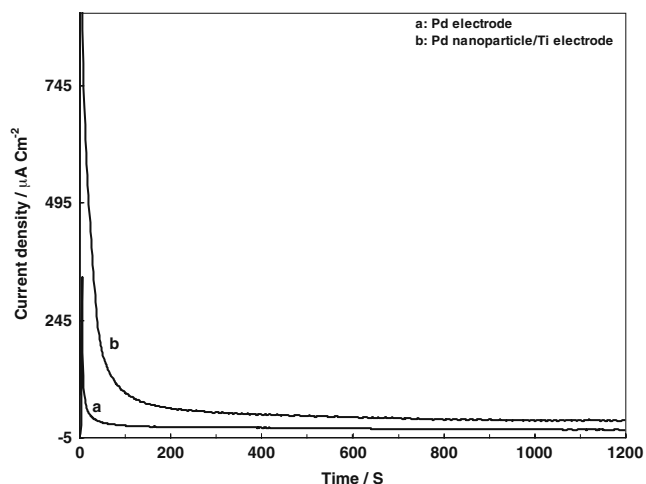


**Fig. 8** Effect of NaOH concentration on 0.1 M methanol electro-oxidation palladium nanoparticles/Ti electrode

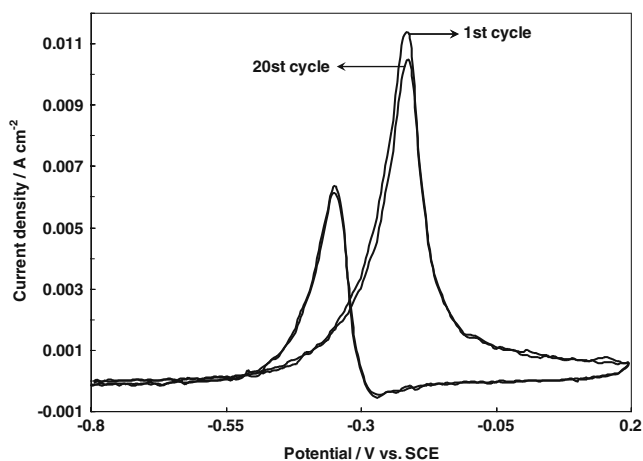
and an enhanced peak current density. The peak potential of methanol oxidation was shifted negatively with increasing the NaOH concentration. The results suggested that the kinetics of the methanol oxidation reaction were improved by the greater availability of  $\text{OH}^-$  ions in solution.

#### Stability of the Pd nanoparticle/Ti electrode

The stability of the palladium nanoparticles/Ti electrode towards methanol oxidation was tested in different ways. Flat Pd electrode and palladium nanoparticles/Ti electrode were subjected with various electrochemical experiments like cyclic voltammetry with multicycles and chronoamperometry. Figure 9 shows the chronoamperograms of flat Pd and palladium nanoparticles/Ti electrodes at 1.0 M NaOH containing 0.1 M methanol aqueous solutions. It is observed that the current density of methanol oxidation on the palladium nanoparticles/Ti electrode keeps higher than that for flat Pd electrode. The current densities decreased and then stabilized over the experimental period. At the end of the experimental period, the current density of palladium nanoparticles/Ti electrode was higher than that of the flat Pd electrode. This implies that the palladium nanoparticles/Ti electrode exhibits higher catalytic activity and better stability than the flat Pd electrodes. In another experiment, the palladium nanoparticles/Ti electrode was cycled in the potential range for methanol oxidation namely  $-0.5$  to  $0.2$  V in alkaline methanol solution for 20 cycles. Figure 10 shows the cyclic voltammograms of methanol electro-oxidation in 1.0 M NaOH containing 0.1 M methanol at a scan rate of  $100 \text{ mV s}^{-1}$ . It can be seen that the peak current density for the twentieth is just 3.1% less than that during the first scan. The result indicates that palladium nanoparticles/Ti electrodes are stable catalysts for methanol



**Fig. 9** Chronoamperograms of flat palladium electrode (a) and palladium nanoparticles/Ti electrode (b) in 1 M NaOH+0.1 M methanol aqueous solutions



**Fig. 10** Stability analysis of palladium nanoparticles/Ti electrode through cyclic voltammetry of 1 M NaOH+0.1 M methanol aqueous solutions for 20 cycles at a scan rate of  $100 \text{ mV s}^{-1}$

oxidation. The steady currents observed on these new electrodes are indicative of the stability of the palladium nanoparticles/Ti and are also in good agreement with this chronoamperometry results.

#### Conclusion

Palladium nanoparticles/Ti electrode excellent electro-catalytic property has been successfully fabricated by electroless plating of palladium on titanium plates. The morphology and surface analysis of palladium nanoparticles/Ti electrodes were investigated by scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. The results indicated that agglomerations containing smaller particles (smaller 5 nm) that formed from combination with others particles and have size about 30–50 nm, are well-dispersed on the surface of titanium plates. The electro-catalytic activity of the palladium nanoparticles/Ti electrode for methanol oxidation was evaluated by cyclic voltammetry and chronoamperometry methods. The palladium nanoparticles/Ti electrode showed much higher currents of methanol oxidation than the flat palladium electrode and the best electro-catalytic activity and stability of palladium nanoparticles/Ti electrode in contrast to the flat palladium electrode were confirmed. Compared to modified carbon electrodes requiring tedious preparations and pretreatment procedures, palladium nanoparticles/Ti electrodes can easily be prepared without any further need to modification, thus from a practical point of view these new electrodes show great prospect in the applications of alcohol fuel cells.

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